

Strong-Coupling Theory of Rattling-Induced Superconductivity

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(Received January 21, 2013)

In order to clarify the mechanism of the enhancement of superconducting transition temperature T_c due to anharmonic local oscillation of a guest ion in a cage composed of host atoms, i.e., *rattling*, we analyze the anharmonic Holstein model by applying the Migdal-Eliashberg theory. From the evaluation of the normal-state electron-phonon coupling constant, it is found that the strong coupling state is developed, when the bottom of a potential for the guest ion becomes wide and flat. Then, T_c is enhanced with the increase of the anharmonicity in the potential, although T_c is rather decreased when the potential becomes a double-well type due to very strong anharmonicity. From these results, we propose a scenario of anharmonicity-controlled strong-coupling tendency for superconductivity induced by rattling. We briefly discuss possible relevance of the present scenario with superconductivity in β -pyrochlore oxides.

KEYWORDS: rattling, superconductivity, heavy electron, cage materials, β -pyrochlore

1. Introduction

Recently, materials with cage structure have attracted much attention in the research field of condensed matter physics from the emergence of exotic magnetism and novel superconductivity. The materials are, for instance, filled skutterudites,¹⁻³⁾ β -pyrochlore oxides,⁴⁻⁷⁾ and clathrate compounds.⁸⁻¹⁰⁾ A common feature of this material group is the existence of nano-size cage composed of relatively light atoms. The ion contained in the cage, frequently called a guest ion, feels a highly anharmonic potential and it can oscillate with large amplitude. Such oscillation of the guest ion in the cage is called *rattling*, which is expected to be an origin of interesting physical properties of cage materials such as magnetically robust heavy electron state of filled skutterudites,¹¹⁾ superconductivity of β -pyrochlore oxides,¹²⁾ and high thermoelectric performance of clathrate compounds.¹³⁾

From a theoretical viewpoint, heavy electron state with phonon origin has been actively investigated in recent years. The magnetically robust heavy electron phenomenon has been discussed from the viewpoint of the Kondo effect with phonon origin.¹⁴⁻¹⁶⁾ The periodic Anderson-Holstein model has been analyzed with the use of a dynamical mean-field theory and a mechanism of the mass enhancement due to large lattice fluctuations and phonon softening towards double-well potential has been addressed.¹⁷⁾ One of the present authors has performed numerical calculations for the Anderson model coupled with local Jahn-Teller and Holstein phonons.¹⁸⁻²¹⁾ From the evaluation of electronic specific heat coefficient γ_e in the Anderson-Holstein model, it has been found that γ_e is enhanced by the rattling, namely, the oscillation of the guest ion in a potential with wide and flat bottom. Then, it has been shown that γ_e enhanced by the rattling is actually robust for an applied magnetic field.²²⁾ Furthermore, it has been pointed out that the Kondo effect due to the rattling exhibits peculiar isotope effect and it can be the experimental evidence for rattling-induced

heavy fermion phenomenon.²³⁾

Now we turn our attention to rattling-induced phenomena in β -pyrochlore oxides AOs_2O_6 ($\text{A}=\text{K}$, Rb , and Cs). It has been observed that T_c increases with the decrease of radius of A ion: $T_c=9.6\text{K}$ for $\text{A}=\text{K}$, $T_c=6.4\text{K}$ for $\text{A}=\text{Rb}$, and $T_c=3.25\text{K}$ for $\text{A}=\text{Cs}$.¹²⁾ The origin of this difference in T_c has been expected to be the anharmonic oscillation of A ion. In fact, it has been revealed that the anharmonicity of the potential for A ion is enhanced when we change A ion in the order of Cs , Rb , and K .²⁴⁾ In particular, KOs_2O_6 has relatively high T_c in comparison with other β -pyrochlore oxides and it exhibits a remarkable first order transition without symmetry change at $T_p = 7.5\text{K}$.²⁵⁾ In β -pyrochlore oxides, characteristic behavior has been observed in the temperature dependence of electrical resistivity²⁶⁾ and NMR relaxation rate.²⁷⁾

These interesting phenomena in β -pyrochlore oxides have been considered to originate from the rattling, i.e., anharmonic oscillation of alkali ion in the cage. Dahm and Ueda have explained unusual temperature dependence of electrical resistivity and NMR relaxation rate by anharmonic phonons.²⁸⁾ Hattori and Tsunetsugu have investigated more realistic model including three dimensional anharmonic phonons in tetrahedral symmetry and have found that T_c is strongly enhanced with increasing the third-order anharmonicity of the potential.^{29,30)} Chang *et al.* have discussed the superconductivity and the first-order transition in KOs_2O_6 by using the strong-coupling Eliashberg approach in the anharmonic Hamiltonian including forth-order terms.³¹⁾ As for the first-order transition observed in KOs_2O_6 , Fuse and Ōno have proposed a possible scenario on the basis of bipolaron formation.³²⁾ From these efforts, it has been gradually recognized that the anharmonic oscillation of the ion in the cage is closely related to the emergence of superconductivity with relatively high T_c . However, the mechanism of the enhancement of T_c due to anharmonicity is still unclear. In particular, it is worth while investigating the relation among T_c , mass enhancement, and anharmonic-

ity in the same model Hamiltonian.

In this paper, we analyze the anharmonic Holstein model in an adiabatic approximation, in order to understand the enhancement of superconducting transition temperature T_c and the electron mass enhancement. For the purpose, we calculate the electron self-energy by using standard Green's function method and evaluate T_c by solving the Eliashberg equation within the Migdal approximation.^{33,34} Due to the evaluation of an effective electron-phonon coupling constant λ_n , it is found that λ_n is increased with the increase of the anharmonicity even if the original electron-phonon coupling is weak. This strong-coupling tendency due to anharmonicity induces the enhancement of electron effective mass and T_c . Then, it is shown that T_c becomes maximum when the guest ion oscillates with large amplitude in a potential with a wide and flat bottom. We also find that the magnitude of T_c is increased with the increase of the Debye-Waller factor, as observed experimentally in β -pyrochlore oxides.

The organization of this paper is as follows. In Sec. 2, we introduce the model Hamiltonian and discuss briefly the relation between potential shape and anharmonicity. Then, we provide the formulation to evaluate electron self-energy and T_c within a framework of the Migdal-Eliashberg theory. In Sec. 3, we show our calculated results and discuss the key role of anharmonicity for the emergence of rattling-induced superconductivity. We also discuss possible relevance of our scenario with experimental results of β -pyrochlore oxides. Finally, we summarize this paper in Sec. 4. Throughout this paper, we use such units as $\hbar=k_B=1$.

2. Model and Formulation

2.1 Anharmonic Holstein Model

Let us introduce the anharmonic Holstein model in which conduction electrons are coupled with local oscillation of guest ion in the anharmonic potential. The Hamiltonian consists of three parts as

$$H = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + H_{\text{eph}} + H_{\text{ph}}, \quad (1)$$

where $\varepsilon_{\mathbf{k}}$ is the energy of conduction electron, \mathbf{k} is momentum, $c_{\mathbf{k}\sigma}$ indicates an annihilation operator of electron with spin σ and momentum \mathbf{k} , H_{eph} indicates the electron-phonon coupling, and H_{ph} is the phonon part. Throughout this paper, we consider a half-filling situation by appropriately adjusting the value of a chemical potential included in $\varepsilon_{\mathbf{k}}$, although we do not explicitly include the chemical potential term in H .

The second term H_{eph} in eq. (1) indicates the electron-phonon coupling part, given by

$$H_{\text{eph}} = g \sum_{\mathbf{i},\sigma} c_{\mathbf{i}\sigma}^\dagger c_{\mathbf{i}\sigma} Q_{\mathbf{i}}, \quad (2)$$

where g denotes an electron-phonon coupling constant, \mathbf{i} indicates an ion site, $c_{\mathbf{i}\sigma}$ is the annihilation operator of electron at a site \mathbf{i} , and $Q_{\mathbf{i}}$ is normal coordinate of oscillation of the guest ion at a site \mathbf{i} . Note here that the reduced mass for the normal oscillation is set as unity in this paper for simplicity.

The third term H_{ph} in eq. (1) denotes the phonon part, written as

$$H_{\text{ph}} = \sum_{\mathbf{i}} [P_{\mathbf{i}}^2/2 + V(Q_{\mathbf{i}})], \quad (3)$$

where $P_{\mathbf{i}}$ denotes the canonical momentum of the guest ion at a site \mathbf{i} and $V(Q_{\mathbf{i}})$ indicates the potential for the guest ion. In order to include the effect of anharmonicity, we express $V(Q_{\mathbf{i}})$ as

$$V(Q_{\mathbf{i}}) = \omega_0^2 Q_{\mathbf{i}}^2/2 + k_4 Q_{\mathbf{i}}^4 + k_6 Q_{\mathbf{i}}^6, \quad (4)$$

where ω_0 is the energy of the guest ion and k_4 and k_6 denote the coefficients for fourth- and sixth-order anharmonic terms, respectively.

For quantum statistical calculations, it is convenient to introduce the annihilation operator of phonon through the standard procedure as $Q_{\mathbf{i}} = (a_{\mathbf{i}} + a_{\mathbf{i}}^\dagger)/\sqrt{(2\omega_0)}$. Then, we obtain H_{eph} and H_{ph} , respectively, as

$$H_{\text{eph}} = \sqrt{\alpha}\omega_0 \sum_{\mathbf{i},\sigma} (a_{\mathbf{i}}^\dagger + a_{\mathbf{i}}) c_{\mathbf{i}\sigma}^\dagger c_{\mathbf{i}\sigma}, \quad (5)$$

and

$$H_{\text{ph}} = \omega_0 \sum_{\mathbf{i}} [a_{\mathbf{i}}^\dagger a_{\mathbf{i}} + 1/2 + \beta(a_{\mathbf{i}} + a_{\mathbf{i}}^\dagger)^4 + \gamma(a_{\mathbf{i}} + a_{\mathbf{i}}^\dagger)^6], \quad (6)$$

where α , β , and γ are given by

$$\alpha = \frac{g^2}{2\omega_0^3}, \quad \beta = \frac{k_4}{4\omega_0^3}, \quad \gamma = \frac{k_6}{8\omega_0^4}, \quad (7)$$

respectively. Note that α is non-dimensional electron-phonon coupling constant, while β and γ indicate non-dimensional fourth- and sixth-order anharmonicity parameters, respectively. By using these non-dimensional parameters, we express the potential as

$$V(q_{\mathbf{i}}) = \alpha\omega_0(q_{\mathbf{i}}^2 + 16\alpha\beta q_{\mathbf{i}}^4 + 64\alpha^2\gamma q_{\mathbf{i}}^6), \quad (8)$$

where $q_{\mathbf{i}} = Q_{\mathbf{i}}/\ell$ and ℓ denotes a typical length scale of the oscillation, given by $\ell = g/\omega_0^2$.

Before proceeding to the formulation, here we briefly discuss how the potential shape is changed by anharmonicity parameters. It is noted that we consider only the case of $\gamma > 0$, since the oscillation of the guest ion should be confined in a finite space of the cage. In order to characterize the potential shape, we define the re-scaled anharmonicity parameter as

$$\beta' = \frac{\beta}{\sqrt{\gamma}}. \quad (9)$$

With the use of this parameter, even if the value of γ is changed, the potential shape can be discussed in the same range of β' . As already mentioned in previous papers,^{22,23,35} the potential shapes are classified into three types by the values of β' as on-center type for $\beta' > -\sqrt{3}/2$, rattling type for $-\sqrt{3}/2 \geq \beta' \geq -1$, and off-center type for $\beta' < -1$. Typical potential shapes are shown in Fig. 1 for various values of β' . Note that the potential height V_0 is defined as the difference between the potential values at local maxima and minima. As a typical example, we show V_0 for the case of $\beta' = -\sqrt{3}/2$. Here we note that $\beta' = -\sqrt{3}/2$ is defined by the value

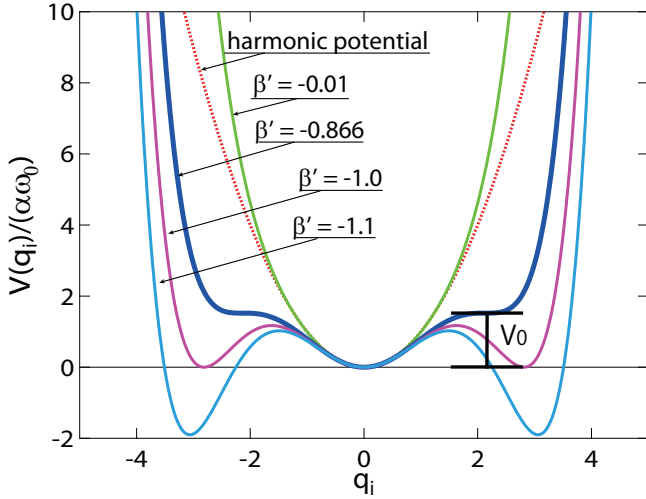


Fig. 1. (Color online) Anharmonic potentials for $\gamma = 10^{-5}$. We show the harmonic potential as a dotted curve for comparison. The curve of $\beta' = -0.01$ denotes the on-center type, while that of $\beta' = -1.2$ indicates the off-center one. As for the meaning of V_0 , see the main text.

at which the potential exhibits saddle points at $q_i \approx \pm 2$, while $\beta' = -1$ indicates the case for which all the potential values at three minima become zeros. It is observed that the rattling-type potential has relatively wide and flat region in the bottom in comparison with other two cases. Namely, in this case, the guest ion is considered to oscillate with large amplitude in the anharmonic potential. From the purpose of this paper, it is quite natural to focus on the parameters around the values for the rattling-type potential.

2.2 Formulation

In order to discuss the superconducting transition temperature T_c , we analyze the Hamiltonian by applying the formalism of the Migdal-Eliashberg theory.^{33,34} First we consider the normal self-energy in the Migdal approximation in which electron-phonon vertex corrections are ignored in an adiabatic limit of $\omega_0 \ll W$, where ω_0 denotes the phonon energy and W is the electron bandwidth. Then, in the second-order perturbation theory in terms of g , the self-energy Σ is given by

$$\Sigma(i\omega_n) = -\alpha\omega_0^2 T \sum_{n'} \sum_{\mathbf{k}'} D_0(i\omega_n - i\omega_{n'}) G(\mathbf{k}', i\omega_{n'}), \quad (10)$$

where T is a temperature, ω_n is the fermion Matsubara frequency defined by $\omega_n = (2n+1)\pi T$ with an integer n , D_0 is the phonon Green's function shown below, and $G(\mathbf{k}, i\omega_n)$ is the electron Green's function, given by

$$G(\mathbf{k}, i\omega_n) = \frac{1}{i\omega_n - \varepsilon_{\mathbf{k}} - \Sigma(i\omega_n)}. \quad (11)$$

We note that the site dependence does not appear in D_0 , since we consider Einstein-type local phonons in the adiabatic approximation. Thus, the self-energy does not depend on the momentum. Note also that in our calculation, we use the bare phonon Green's function D_0 , instead of dressed phonon Green's function D , since we

consider an adiabatic situation in which W is much larger than the phonon energy ω_0 .

Concerning the phonon Green's function D_0 of anharmonic system, it is convenient to express it in the spectral representation as

$$D_0(i\nu_n) = \int \frac{\rho_{\text{ph}}(\omega)}{i\nu_n - \omega} d\omega, \quad (12)$$

where ν_n is the boson Matsubara frequency defined by $\nu_n = 2n\pi T$, and $\rho_{\text{ph}}(\omega)$ is phonon spectral function, given by

$$\rho_{\text{ph}}(\omega) = \sum_{i,j} A_{i,j} \delta(\omega + E_i - E_j). \quad (13)$$

Here E_i is the i -th eigenenergy of H_{ph} and the spectral weight $A_{i,j}$ is given by

$$A_{i,j} = \frac{1}{\Omega} (e^{-E_i/T} - e^{-E_j/T}) |\langle \Phi_i | u_i | \Phi_j \rangle|^2, \quad (14)$$

where $|\Phi_i\rangle$ is the i -th eigenstate of H_{ph} , Ω is the partition function, given by $\Omega = \sum_i e^{-E_i/T}$, and u_i is the non-dimensional displacement operator, given by $u_i = a_i + a_i^\dagger$.

Let us define an electron mass enhancement factor Z , given by

$$Z = 1 - \frac{\Sigma(i\pi T)}{i\pi T}. \quad (15)$$

We note that the effective mass m^* is given by $m^* = Zm$, where m is bare electron mass. Here we assume that Z is given by the difference of Σ on the imaginary axis at the lowest temperature, although Z should be defined by the energy differentiation of Σ on the real axis as

$$Z = 1 - \left. \frac{\partial \text{Re} \Sigma(\omega)}{\partial \omega} \right|_{\omega=0}, \quad (16)$$

where $\Sigma(\omega)$ denotes the electron self-energy on the real axis and ω denotes the energy. Since $\Sigma(\omega)$ is found to exhibit a peak in the order of the phonon energy ω_0 , we replace the energy differentiation with the energy difference of the width T for $T < \omega_0$.³⁵ In this paper, we are interested in the quantity around $T = T_c$ and T_c is considered to be lower than ω_0 . Thus, we adopt the present definition for Z .

For the purpose to evaluate T_c , we solve the linearized gap equation at $T = T_c$, given by

$$\phi(i\omega_n) = \alpha\omega_0^2 T \sum_{n'} \sum_{\mathbf{k}'} D_0(i\omega_n - i\omega_{n'}) F(\mathbf{k}', i\omega_{n'}), \quad (17)$$

where $\phi(i\omega_n)$ is anomalous self-energy and $F(\mathbf{k}, i\omega_n)$ is anomalous Green's function, given in the linearized form in the vicinity of T_c as

$$F(\mathbf{k}, i\omega_n) = -G(\mathbf{k}, i\omega_n) G(-\mathbf{k}, -i\omega_n) \phi(i\omega_n). \quad (18)$$

Note that here we assume the isotropic s -wave gap, since we consider Cooper pairs mediated by phonons. Thus, the momentum dependence is suppressed in the anomalous self-energy.

The calculation procedure is as follows: First we determine the normal self-energy by solving self-consistently eqs. (10) and (11). Then, by using the obtained normal self-energy, we solve the gap equation eqs. (17) and (18).

Note that T_c is determined as a temperature at which the positive maximum eigenvalue of the gap equation becomes unity.

In the actual calculations, we assume the electron density of states with rectangular shape of the electron bandwidth W . Hereafter W is taken as the energy unit and we set $W = 1$. For the sum on the imaginary axis, we use 32768 Matsubara frequencies. In order to accelerate the actual calculations in eqs. (10) and (17), we exploit a Fast-Fourier-Transformation algorithm for the summation in terms of n' . The eigenvalue of the gap equation is obtained with the use of the power method. For diagonalization of H_{ph} , we use 250 phonon basis. Note that we have checked the convergence of the eigenenergy by comparing the results obtained by using 300 phonon basis. Throughout this paper, we set $\omega_0 = 0.1$ and $\lambda = 0.5$, where λ is the Eliashberg electron-phonon coupling constant given by $\lambda = 2\alpha\omega_0/W$.

3. Calculated Results

3.1 Superconducting transition temperature

Let us first discuss the effect of anharmonicity on the superconducting transition temperature T_c . In Fig. 2(a), we depict three curves of T_c vs. β' for $\gamma=0.01$, 0.001, and 0.0001. For $\gamma=0.0001$, T_c slowly increases with the decrease of β' in the range of $\beta' > -1$ and it rapidly decreases at $\beta' = -1$. Note that we could not calculate T_c smaller than 0.001 due to the limitation of the present numerical calculations. For $\gamma = 0.001$, we also observe that T_c is enhanced by the increase of fourth-order anharmonicity and it takes the largest value at $\beta' \simeq -1$. Note that the largest value is also the highest among those in three curves. In the parameter region of the off-center type potential, T_c rapidly decreases.

For $\gamma = 0.01$, T_c also exhibits a peak structure, but the width of the peak is broad and T_c becomes highest for $\beta' \approx -1.2$. As understood from Fig. 1, the potential is the off-center type with a couple of shallow minima at $q_1 \approx \pm 2$. Although T_c is not always maximum just in the range of $-1 < \beta' < -\sqrt{3}/2$, we conclude that the highest T_c is obtained in the vicinity of the rattling potential with a wide and flat bottom.

In order to consider further the mechanism of the increase of T_c , we estimate the effective electron-phonon coupling constant λ_n at $T = T_c$. With the use of the phonon spectral function $\rho_{\text{ph}}(\omega)$, λ_n is evaluated as

$$\lambda_n = \frac{\lambda\omega_0}{2} \int_{-\infty}^{\infty} \frac{\rho_{\text{ph}}(\omega)}{\omega} d\omega. \quad (19)$$

For the case of $\beta=\gamma=0$ (harmonic phonon), we easily obtain $\lambda_n=\lambda$ from the definition of λ_n and the phonon spectral function. Note, however, that in general, λ_n is different from λ . Thus, the difference between λ_n and λ is considered to indicate the effect of anharmonicity on the electron-phonon coupling constant.

The calculated results for λ_n are shown in Fig. 2(b). We immediately observe that in the on-center type potential ($\beta' > -\sqrt{3}/2$), λ_n is not so enhanced from the bare value of λ . When β' enters the value of the region of the rattling-type potential ($-\sqrt{3}/2 \geq \beta' \geq -1$), λ_n is

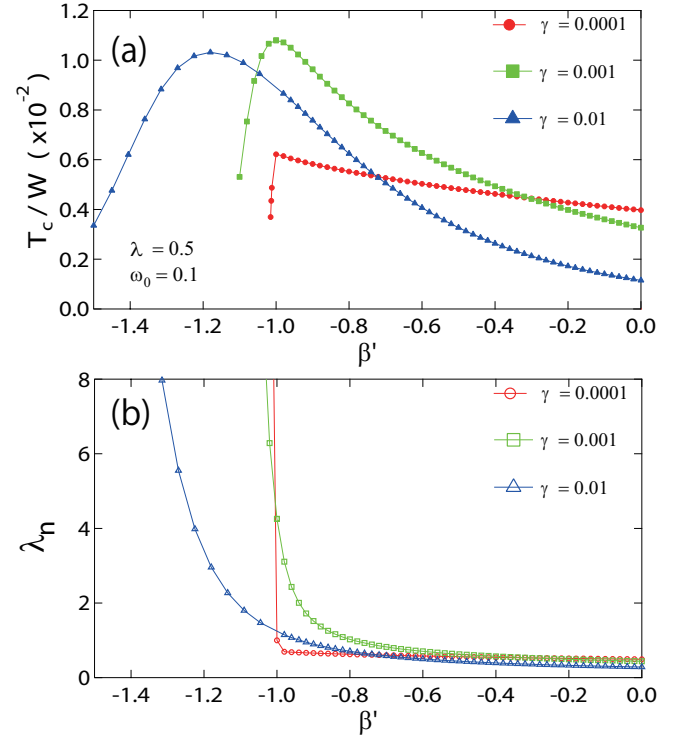


Fig. 2. (Color online) (a) Superconducting transition temperature T_c vs. β' for $\gamma=0.01$, 0.001, and 0.0001. Here we set $\lambda = 0.5$ and $\omega_0 = 0.1$. (b) Effective electron-phonon coupling constant λ_n vs. β' for the same parameters as in the panel (a).

rapidly increased with the decrease of β' . When we further decrease the values of β' , λ_n continues to increase even in the off-center type potential ($\beta' < -1$). Here we should pay due attention to the validity of the present adiabatic approximation in the off-center type potential, but this point will be commented later. At the present stage, we suggest that the enhancement of T_c is related to the strong coupling state due to anharmonicity.

Concerning the formation of the peak in T_c , we provide a qualitative comment from the strong-coupling effect. In the BCS theory, it is well known that T_c is expressed as $T_c = 1.13\omega_0 e^{-1/\lambda}$. When we consider the renormalization effect, the formula of T_c is changed as $T_c = 1.13\omega_0 e^{-Z/\lambda_n}$, where Z is the mass enhancement factor. Namely, $1/Z$ indicates the renormalization effect. Note that when λ_n is moderately large, Z is roughly given by $1 + \lambda_n$, leading to the simplest version of the McMillan formula.³⁶⁾ When λ_n is small, the renormalization effect is not so significant and the increase of λ_n contributes to the enhancement of T_c . On the other hand, when λ_n becomes much larger than unity, the renormalization effect should be dominant and it rather suppresses the value of T_c . Thus, the peak is formed in T_c as a function of β' .

3.2 Phonon softening due to anharmonicity

In the previous subsection, it has been clarified that the enhancement of T_c is triggered by the strong-coupling tendency due to anharmonicity. Next we attempt to understand the origin of such tendency. For the purpose, let us examine the change of the phonon spectral func-

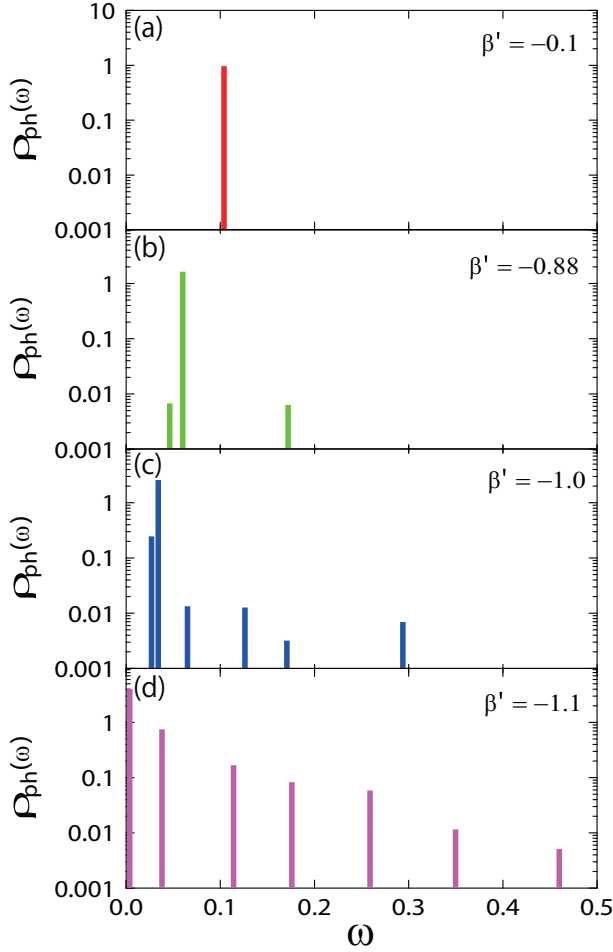


Fig. 3. (Color online) Phonon spectral function $\rho_{\text{ph}}(\omega)$ vs. energy ω for (a) $\beta' = -0.1$, (b) $\beta' = -0.88$, (c) $\beta' = -1.0$, and (d) $\beta' = -1.1$. Other parameters are set as $\lambda = 0.5$, $\omega_0 = 0.1$, and $\gamma = 0.001$. Note that we calculate $\rho_{\text{ph}}(\omega)$ at $T = T_c$.

tion, when we change the value of β' . In Figs. 3, we depict $\rho_{\text{ph}}(\omega)$ for $\beta' = -0.1, -0.88, -1.0$, and -1.1 at $T = T_c$ with $\lambda = 0.5$, $\omega_0 = 0.1$, and $\gamma = 0.001$. The panel (a) for $\beta' = -0.1$ indicates the results for the on-center type potential. We observe that the phonon spectral function is quite similar to that of the harmonic phonons with a finite weight at $\omega = \omega_0$. Then, λ_n for this case is almost equal to λ , as observed in Fig. 2(b).

When we decrease the value of β' , the phonon state with finite weights are gradually shifted to zero, as observed in Figs. 3(b) and 3(c), which are the results for the rattling-type potential. It is easy to understand that λ_n becomes large, since low-energy phonon states with finite weights contribute to λ_n through $\rho_{\text{ph}}(\omega)/\omega$ in eq. (19). In Fig. 3(d) for the case of $\beta' = -1.1$, the largest weight of $\rho_{\text{ph}}(\omega)$ shifts to the lower energy and the moderate weights appear in higher ω . Thus, λ_n becomes large in the parameter region of the off-center type potential. In short, the increase of the anharmonicity leads to phonon softening. Namely, the weight of $\rho_{\text{ph}}(\omega)$ is shifted to lower energy and thus, λ_n is enhanced in the anharmonic potential. Note that our conclusion is consistent with the previous result.¹⁷⁾

Next we discuss the phonon excitation in order to un-

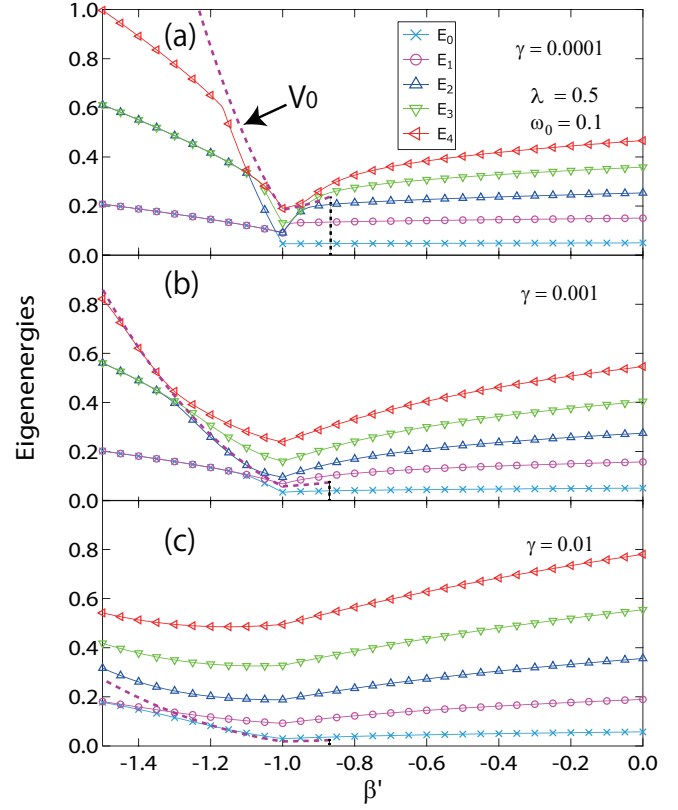


Fig. 4. (Color online) Five lowest eigenenergies $E_0 \sim E_4$ (solid curves with symbols) and V_0 vs. β' for (a) $\gamma = 0.01$, (b) 0.001 , and (c) 0.0001 . Note that we do not show all eigenenergies in these figures. We set $\lambda = 0.5$ and $\omega_0 = 0.1$. Since V_0 does not exist for $\beta' > -\sqrt{3}/2$ due to its definition, V_0 is depicted in the region of $\beta' \leq -\sqrt{3}/2$.

derstand the relation between T_c and anharmonic oscillation. In Figs. 4(a)-4(c), we depict eigenenergies $E_0 \sim E_4$ of H_{ph} and V_0 for $\gamma = 0.0001, 0.001$, and 0.01 , respectively. First let us consider overall tendency of the change of eigenenergy due to the anharmonicity found in Figs. 4(a)-4(c). In the case of the on-center type potential for $\beta' > -\sqrt{3}/2$, all eigenenergies are gradually decreased with the decrease of β' . For $-1.0 < \beta' < -\sqrt{3}/2$, in which we observe the rattling-type potential, the width between eigenenergy levels becomes small. This is the origin of the shift of phonon spectral function, as observed in Fig. 3. For $\beta' < -1.0$, the eigenenergies become doubly degenerate, which is originating from the left and right deep minima in the off-center type potential. The width between degenerate energy levels are rather large, when we further decrease β' , but the degenerate phonon states lead to the strong coupling state in the present adiabatic approximation. This point will be commented later.

Intuitively, the phonon softening due to anharmonicity is understood from the energy of oscillator confined in a potential. If the potential size becomes wide, the momentum of the oscillator becomes small and the kinetic energy is suppressed due to the well-known uncertainty principle. In the present case, the size of the potential bottom is effectively enlarged due to the anharmonicity and thus, the typical phonon energy is suppressed due to

the quantum effect. We believe that it is the main effect of anharmonicity on the electron-phonon coupling state.

Next we turn our attention to the change of V_0 , since V_0 competes with the zero-point energy E_0 . Note again that V_0 is defined as the difference between the potential values at local maxima and minima. From the competition between V_0 and E_0 , we can discuss the quantum effect of potential shape, when there exists structure in the bottom of the potential. For $\gamma=0.0001$ in Fig. 4(a), since V_0 is always larger than E_0 and E_1 , the guest ion oscillates in the narrow width of the potential bottom, which is almost the same as that of the harmonic potential in the low-temperature region. On the other hand, for $\beta' < -1.0$, since the phonon energies are degenerate, the oscillation state is drastically changed from the small oscillation at the potential minimum to the quantum tunneling or thermal activation between two potential minima. Thus, the behavior of T_c is rapidly changed at $\beta' = -1.0$ in the present calculations. For $\gamma=0.001$ in Fig. 4(b), V_0 is close to E_0 at $\beta' \simeq -1.0$, corresponding to the peak observed in the curve for T_c in Fig. 2(a). For $\gamma=0.01$, V_0 crosses E_0 at $\beta' \simeq -1.2$, which also corresponds to the peak position in T_c .

From these results, we consider that the behavior of T_c is closely related to E_0 and V_0 . For $\gamma=0.001$ and 0.01 , it is found that T_c takes the maximum value at the parameters corresponding to $E_0 \simeq V_0$. In this case, the oscillation amplitude of guest ion is rapidly increased, since the ion can feel the potential structure in the energy region less than the zero-point energy. Namely, the condition of $E_0 \simeq V_0$ just indicates the rattling oscillation of the guest ion. Then, T_c is considered to take the maximum value in the rattling type potential.

Hattori and Tsunetsugu have discussed the variation of T_c by using three-dimensional anharmonic phonons in the tetrahedral symmetry.³⁰⁾ They have found a crossover in the energy spectrum to the quantum tunneling regime and T_c becomes large at the crossover point. We consider that their condition of the crossover point corresponds to $E_0 \simeq V_0$. Thus, our result is consistent with the previous study.

3.3 Zero-point energy and anharmonicity

Now we focus on the relation between the zero-point energy E_0 and the potential height V_0 . When the local maximum dose not exist for $\beta' = -\sqrt{3}/2$, V_0 is defined by the potential height at the saddle point. For $-\sqrt{3}/2 < \beta'$, V_0 cannot be defined. It should be noted that E_0 is the lowest energy for the oscillation of the guest ion.

For the rattling-type potential, the potential has minimum at $q_1 = 0$. At low temperatures, for $E_0 < V_0$, the guest ion oscillates in the narrow width of the potential bottom, which is almost the same for that of the harmonic potential. On the other hand, for $E_0 > V_0$, the guest ion can oscillate with large amplitude, since the potential is wide for the energy larger than V_0 . Also in the off-center type potential, for $E_0 > V_0$, the guest ion can oscillate with large amplitude, since the structure at the bottom is masked by the zero-point energy. However, for $E_0 < V_0$, the guest ion oscillates in one of potential

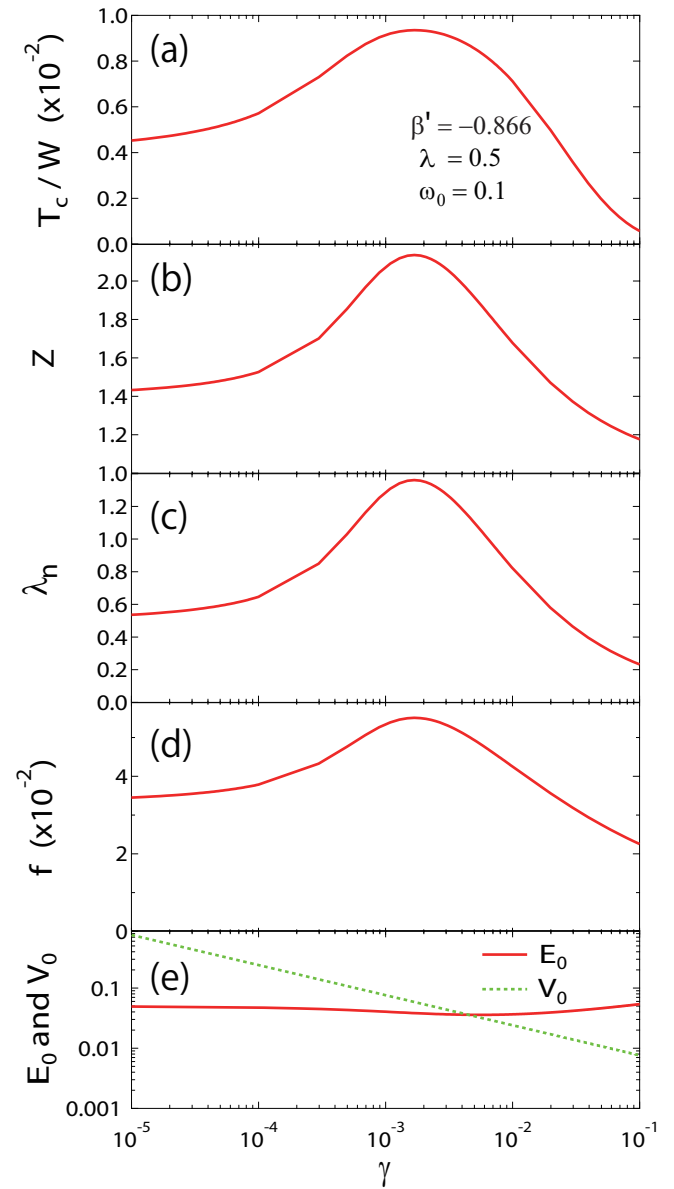


Fig. 5. (Color online) (a) Superconducting transition temperature T_c vs. γ . (b) Mass enhancement factor Z vs. γ . (c) Effective electron-phonon coupling constant λ_n at $T = T_c$ vs. γ . (d) Non-dimensional Debye-Waller factor f vs. γ . (e) The zero-point energy E_0 and the potential height at the saddle point V_0 vs. γ . For these panels, we always keep the relation of $\beta' = -\sqrt{3}/2$. Other parameters are set as $\lambda=0.5$ and $\omega_0=0.1$.

minima and sometimes moves to other potential minima due to quantum tunneling effect. Thus, it is considered that the oscillation of the guest ion in the anharmonic potential is quite different between two cases of $E_0 > V_0$ and $E_0 < V_0$.

Here let us discuss T_c by focusing on the potential at $\beta' = -\sqrt{3}/2$, which is depicted by thick curve in Fig. 1. Note again that V_0 is the potential height at the saddle point in this case and β depends on γ through the relation of $\beta = -\sqrt{3}\gamma/2$. In Figs. 5(a)-5(c), we depict γ dependence of T_c , Z , and λ_n , respectively. When we increase the value of γ from 10^{-5} , all those values are increased, but they turn to be decreased to form peaks at a certain value of γ , which is defined as γ^* .

In order to elucidate the relation with the amplitude of the guest ion, we evaluate the Debye-Waller factor which represents the intensity of thermal motion. In the non-dimensional form, it is given by

$$f = \frac{F_{\text{DW}}}{|\mathbf{G}|^2 \ell^2} = \frac{\langle Q_i^2 \rangle}{3\ell^2}, \quad (20)$$

where F_{DW} denotes the Debye-Waller factor, \mathbf{G} denotes the reciprocal lattice vector, ℓ is the typical length scale defined by $\ell = g/\omega_0^2$, and $\langle \dots \rangle$ denotes the operation to take thermal average. In Fig. 5(d), we show the result for f . We find that f exhibits the peak structure which is quite similar to those in Figs. 5(a)-5(c). Namely, f is closely related to the behavior of T_c , Z , and λ_n .

In Fig. 5(e), we depict two curves of E_0 and V_0 . At $\gamma = \gamma^*$, they cross with each other, so that the guest ion oscillates with large amplitude in the case of $E_0 \simeq V_0$. Thus, the large amplitude of the guest ion leads to the strong coupling state and the enhancement of T_c . In addition, it is found that this oscillation causes the heavy electron state. This is consistent with our previous result.³⁵⁾

3.4 Debye-Waller factor and T_c

Let us now try to understand the tendency of the variation of T_c experimentally observed in β -pyrochlore oxides AOs_2O_6 ($A = \text{K}, \text{Rb}, \text{Cs}$) by focusing on the Debye-Waller factor at the room temperature and the anharmonicity.

First we briefly summarize the experimental facts for β -pyrochlore oxides. The isotropic atomic displacement parameter U_{iso} at the room temperature which corresponds to the Debye-Waller factor in our calculation increases as $2.5 \times 10^{-4} \text{nm}^2$, $3.41 \times 10^{-4} \text{nm}^2$, and $7.4 \times 10^{-4} \text{nm}^2$ in the order of decreasing ionic radius, i.e., Cs, Rb, and K.¹²⁾ On the other hand, T_c and λ_n for β -pyrochlore oxides are summarized as $T_c = 3.25 \text{ K}$ and $\lambda_n = 2.76$ for Cs, $T_c = 6.4 \text{ K}$ and $\lambda_n = 3.38$ for Rb, and $T_c = 9.6 \text{ K}$ and $\lambda_n = 6.3$ for K. Note that the experimental value of λ_n is obtained by $1 + \lambda_n = \gamma_{\text{exp}}/\gamma_b$, where γ_{exp} is the experimental Sommerfeld constant and γ_b is evaluated by the band-structure calculations. Moreover, Kuneš *et al.* have clarified that the anharmonicity of the potential which A ion feels increases in the order of Cs, Rb, and K.²⁴⁾ Thus, in β -pyrochlore oxides, T_c and λ_n are closely related to the anharmonicity.

In Figs. 6(a) and 6(b), we show the calculated results of T_c vs. f and λ_n vs. f , respectively. Here we change the anharmonicity parameters (β, γ) on the straight line which connects the points of $(\beta, \gamma) = (-0.00392, 0.00154)$ and $(-0.00253, 0.00451)$. Namely, since the non-dimensional anharmonicity parameter β' is changed from -0.35 to -1.0 , the potential shape is changed from on-center type to rattling one. It is understood that when f is increased, both T_c and λ_n are increased. This tendency agrees well with the experimental situation. Note that it is easy to find other parameter regions to depict the figure similar to Fig. 6. It is concluded that in the rattling potential with large amplitude of the guest ion, T_c and the mass enhancement is increased with the increase of the Debye-

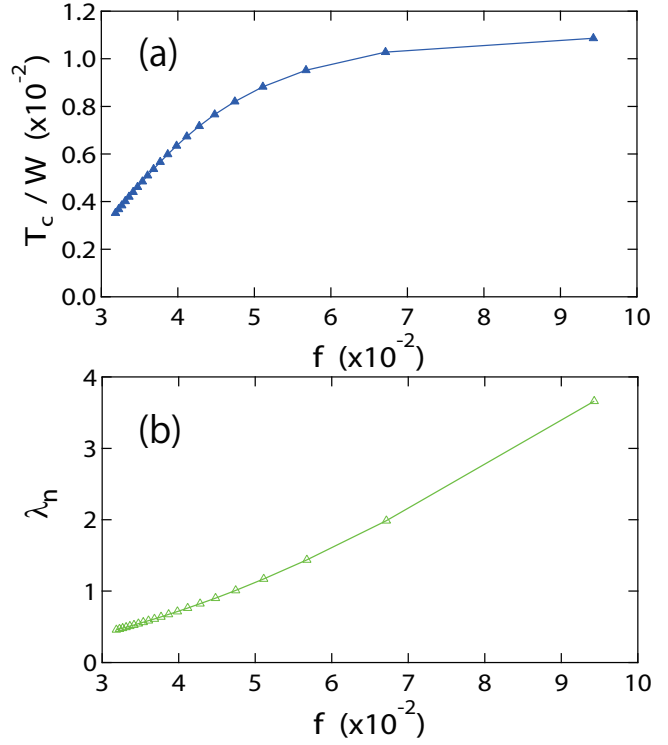


Fig. 6. (Color online) (a) Superconducting transition temperature T_c vs. f and (b) λ_n vs. f . Concerning the parameters to depict these curves, see the main text.

Waller factors, as observed in β -pyrochlore oxides.

4. Discussion and Summary

In this paper, we have analyzed the anharmonic Holstein model which describes the coupling of conduction electrons with local ion oscillations in the potential with fourth- and sixth-order anharmonic terms, in order to understand the enhancement of T_c due to anharmonicity. First we have investigated T_c and the effective electron-phonon coupling constant λ_n . Then, we have found that T_c is enhanced by the strong coupling tendency due to anharmonicity. When the guest ion oscillates with large amplitude, the phonon softening occurs. The phonon spectral weights are shifted towards lower energy and the strong coupling situation is realized even if we consider originally the weak-coupling case. This strong-coupling tendency due to anharmonicity is considered to be a route to arrive at high T_c . We believe that this type of strong-coupling superconductivity is realized in β -pyrochlore oxides. The relation between T_c vs. f as well as λ_n vs. f seems to support our present proposal.

In the present calculation, we have always used the same phonon energy ω_0 , but in actuality, ω_0 is different from material to material. The energy of A ion has been reported in the specific heat measurements,³⁷⁾ the Raman scattering experiment³⁸⁾ and the neutron scattering experiment.^{39,40)} Nagao *et al.* have reported that the energies of the oscillator are 75.1K for $A=\text{Cs}$, 66.4K for $A=\text{Rb}$, and 22K and 61K for $A=\text{K}$ in β -pyrochlore oxides AOs_2O_6 .³⁷⁾ If the oscillation energy for the case of $A=\text{K}$ is taken as 61K, roughly speaking, it is validated to use

the same ω_0 for three β -pyrochlore oxides. However, if we pay our serious attention to the phonon energy of 22K, we should consider a situation in which the oscillators for A=Cs and Rb have same energy, while the energy for A=K is smaller than it. If we attempt to pursue quantitative agreement with the experimental facts, it may be necessary to consider the difference among materials. However, the research along such a direction should be done with the use of more realistic model. It is one of future problems.

In the present adiabatic calculations, λ_n is monotonically increased with the decrease of β' , as shown in Fig. 2(b). We consider that the calculations are valid for the on-center type, the rattling-type, and the off-center type potential with shallow minima. However, when the value of λ_n is enhanced in the off-center type potential with deep minima at non-zero q_i 's, another effect should be significant. Namely, for large λ_n , the effective bandwidth given by W/Z becomes comparable with the phonon energy and the adiabatic condition will be violated. Thus, in the strong-coupling region, it is essential to include the non-adiabatic effect through electron-phonon vertex corrections. When we include such non-adiabatic effect, the degeneracy in phonon energy originating from the right and left positions of the off-center type potential will be lifted by the electron-phonon coupling. In the present calculation, unfortunately, the vertex corrections are not included and the results in the region of $|\beta'| \gg 1$ with negative β' should be reconsidered with the inclusion of the vertex corrections. This is another future task.

In summary, we have found that the large amplitude anharmonic oscillation induces the enhancement of T_c and the heavy electron state through the strong-coupling tendency controlled by the anharmonicity. We have shown that when the Debye-Waller factor is increased, both T_c and λ_n are increased. This tendency agrees qualitatively well with the experimental facts in β -pyrochlore oxides.

Acknowledgment

The authors thank T. Fuse for discussions on rattling phenomena. This work has been supported by a Grant-in-Aid for Scientific Research on Innovative Areas "Heavy Electrons" (No. 20102008) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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